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Citation: Journal of Applied Physics **113**, 187208 (2013); doi: 10.1063/1.4801964
View online: http://dx.doi.org/10.1063/1.4801964
View Table of Contents: http://aip.scitation.org/toc/jap/113/18
Published by the American Institute of Physics

JOURNAL OF APPLIED PHYSICS 113, 187208 (2013)

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(Received 15 October 2012; accepted 4 January 2013; published online 8 May 2013)

The temperature and bias field dependences of macroscopic, measured by pulsating load method, and local, measured by piezoresponse force microscopy, longitudinal piezoelectric responses have been studied in (001)-oriented flux-grown $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$ $xPbTiO_3$ $(0.0 \le x \le 0.29)$ single crystals. Both types of responses exhibit a dramatic enhancement with increasing bias fields. At the same time, their temperature maxima shift from the Vogel-Fulcher temperature to the vicinity of the dielectric permittivity maximum, where the critical point in the *E-T* phase diagram is located. Both datasets confirm a quasicritical nature of the giant field-induced piezoelectric response in relaxor single crystals. © *2013 AIP Publishing LLC* [http://dx.doi.org/10.1063/1.4801964]

INTRODUCTION

The solid solutions between disordered relaxor lead magnesium niobate and ferroelectric lead titanate $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ (PMN-*x*PT) have attracted significant attention because of their remarkable dielectric, electrostrictive, and piezoelectric properties that have extremely wide applications nowadays.[1–3] First-principles calculations have related outstanding electromechanical properties of PMN-*x*PT to the polarization rotation.[4] It was shown recently that the piezoelectric properties of PMN-*x*PT can be enhanced even further if one applies an electric field moving the system towards a critical point.[5] The critical point has been found experimentally in both pure PMN[6,7] and PMN-*x*PT crystals with $x = 0.06$ 0.295.[7–9] Recently a quasicritical behavior of the field-induced pyroelectric response was observed in PMN-0.2PT single crystals[10] and some PMN-*x*PT ceramics.[11] This finding helps to understand the nature of a dramatic enhancement of the pyroelectric coefficient observed earlier for different PMN-*x*PT compositions under a bias field.[12,13]

It is worth noting that a quasicritical nature of the piezoelectric response has been experimentally confirmed only by the measurements of a macroscopic transversal piezoelectric effect, namely when piezoelectric coefficient d_{31} was measured by the resonance-antiresonance method.[5–9] In this context, the scope of the present paper is a comparative study of the bias field effect on macroscopic direct and local converse longitudinal piezoelectric response of (001)-oriented flux-grown PMN-*x*PT single crystals.

EXPERIMENTAL

Single crystals of PMN *x*PT $(0.0 \le x \le 0.29)$ were grown in the Research Institute of Physics (Southern Federal University, Rostov-on-Don, Russia) using spontaneous crystallization from a PbO B_2O_3 flux.[14] The crystals had a yellow color, the cubic shape with the edge lengths up to 6 mm, and cube faces parallel to the {001} planes related to the perovskite unit-cell axes. The stoichiometry of the single crystals was confirmed using the X-ray microanalyser "Camebax Micro." Polished plates (0.5 1.0 mm thick) cut along the (001) perovskite plane and electroded with sputtered Pt were used for measurements. The dielectric study was performed at the 2 K/min heating/cooling rate using a computer-controlled impedance analyzer E7-20.

The macroscopic piezoelectric longitudinal coefficient d_{33} was measured by the method of a weak pulsating load at the frequency of 120 Hz on slow heating at a rate of 0.5 K/min. The samples were previously poled on cooling under the electric field $E > E_c$, where E_c is the coercive field determined from the hysteresis loop. The poling procedure was performed from the temperature exceeding the temperature T_m of the dielectric permittivity maximum by 20 50 K, to the temperature $T \ll T_m$. A uniaxial mechanical load produced by a generator and vibrator was transmitted via a ceramic rod to the studied sample. A value of the alternating pressure, $P_{max} = 64$ kPa, applied to the sample was controlled using a tensometric pickup based on a quartz element. The alternating electric signal generated by the sample was detected and amplified by a synchronized detector UPI-1. The temperature was controlled with accuracy of up to 0.2 K.

The measurements of the local converse longitudinal piezoelectric response were carried out by piezoresponse force microscopy (PFM).[15] This method is widely used for imaging of ferroelectric domains and manipulation of polarization at the nanoscale. It has also been successfully applied for the investigation of relaxors.[16] The $d_{33}(V)$ dependences can be measured by applying to the PFM tip sequences of voltage pulses with variable height and acquiring the piezoelectric response during or after each pulse.

A commercial SPM (Bruker, Multimode, Nanoscope IIIA) was used for the PFM measurements. The microscope was equipped with a lock-in amplifier (Stanford Research, SR-830) and a function generator (FG120, Yokogawa), which were used to apply the *ac* and *dc* voltages to the crystal for both imaging and local hysteresis loop measurements. The amplitude and frequency of the probing *ac* voltage were 1 2 V and 50 kHz, respectively. The *dc* voltage was varied from −40 to 40 V. Conducting n-doped Si cantilevers (PPP-NCHR, Nanosensors) with the resonance frequency of 330 kHz and the tip apex radius about 10 nm were used. The local hysteresis measurements were performed in the so-called "step" mode, when the piezoresponse is measured after the *dc* pulse to avoid a contribution due to the electrostatic effect.[17]

Measurements of local piezoresponse as a function of temperature were carried out in the course of cooling after preliminary heating to $T > T_m$. After the measurement at a higher temperature have been finished, the sample was cooled to the next measuring point and held there for 1-1.5 h for equilibration before the next measurement.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the dielectric permittivity and macroscopic direct longitudinal piezoelectric coefficient d_{33} for (001) oriented PMN *x*PT single crystals with different Ti content. Measurements of the piezoelectric coefficient have been carried out on the preliminary poled samples either at zero bias or under a bias field approximately corresponding to the critical field E_{cr} for the composition studied. The E_{cr} values were estimated from the (*E*,*T*)-phase diagrams plotted using the results of dielectric, pyroelectric, and optical studies.[8,18] One can see that at a zero bias field the piezoelectric coefficient has the maximum near

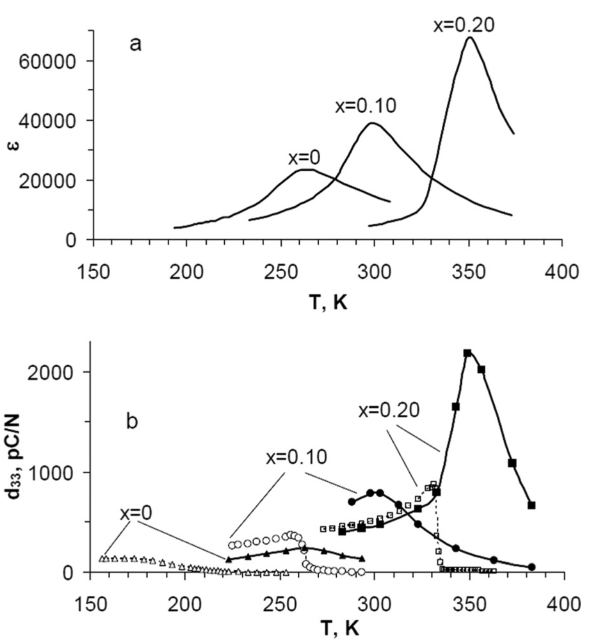

FIG. 1. Temperature dependences of (a) dielectric permittivity measured at 1 kHz and (b) macroscopic direct longitudinal piezoelectric coefficient d_{33} for (001) oriented (1 *x*)Pb($Mg_{1/3}Nb_{2/3}$)O_3 *x*$PbTiO_3$ single crystals. Numbers at the curves correspond to *x* values. Measurements of the piezoelectric coefficient have been carried out after preliminary polarization of single crystals either at zero bias (empty symbols) or under a bias field (solid symbols) having the values of 3 kV/cm (*x* 0 and 0.10) or 1.2 kV/cm (x 0.20).

the Vogel-Fulcher (VF) temperature, T_f, i.e., much lower than the dielectric permittivity ε maximum temperature T_m. The VF or freezing temperature is a characteristic temperature of relaxors. Usually it is estimated from a fitting of the frequency dispersion of T_m by the empirical Vogel-Fulcher law, $f = f_0 \exp[-E_a/k(T_m(f) - T_f)]$, where parameters f_0 and E_a have meaning of the attempting frequency and activation energy, respectively. The VF behavior is usually attributed a slowing down of dynamics of polar nanoregions (PNRs) accompanied by a strong broadening of the relaxation time spectrum, whose slowest end or even mean extends into the regime of macroscopic times at T_f.[19] Pirc and Blinc have proposed that the principal mechanism responsible for freezing in relaxors appears to be the growth and percolation of PNR clusters culminating in the formation of an infinite cluster at T_f.[20] At the same time, T_f has been found to correspond to collapse of the field induced macroscopic polarization when measuring at zero-field on heating.[19] This can be a reason why the piezoelectric response of the poled samples exhibits a maximum in vicinity of T_f (Figure 1). Under bias field, this maximum grows in magnitude and shifts to temperature close to T_m, i.e., to the position of the supposed critical point in the (*E*,*T*)-phase diagram.[8,18]

Figure 2 shows local piezoresponse hysteresis loops measured at room temperature in the PMN-*x*PT single crystals with different compositions. In each experiment two hysteresis loops were measured successively. Comparison between them manifests a good reproducibility of data. One can see that increasing of titanium content results in change of the hysteresis loops shape from tilted slim-like one common for relaxors to rectangular one typical for ferroelectrics. For both PMN and PMN-0.1PT the Vogel-Fulcher temperature, which corresponds to slowing down of dynamics of PNRs, lies below room temperature. It was argued that in such case two polarization components coexist in relaxors: static and dynamic ones related to the mesoscopic labyrinthine domains and still dynamic PNRs, respectively.[21] In PFM experiments an applied electric field does not affect substantially the static

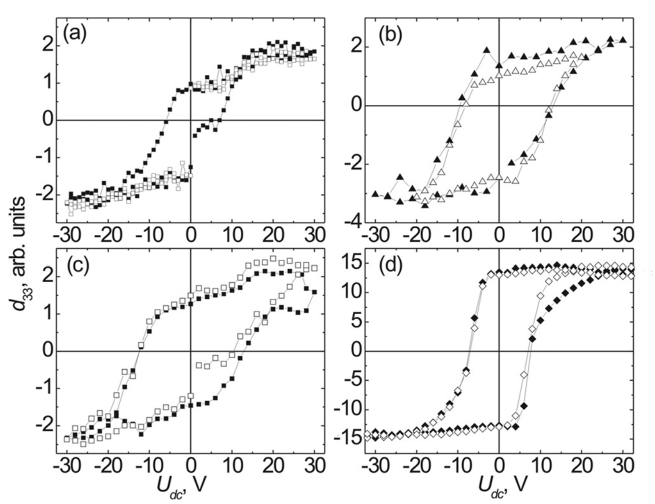

FIG. 2. Local converse longitudinal piezoresponse hysteresis loops for PMN (a), PMN 0.1PT (b), PMN 0.2PT (c), and PMN 0.29PT (d) single crystals measured by PFM in the step mode at room temperature. Two successively measured hysteresis loops are shown: open and solid symbols correspond to the 1st and 2nd run, respectively.

component of polarization, but the induced piezoresponse is mainly due to alignment of dynamic PNRs by the field.[21–23] After the bias field is switched off, the induced PFM signal relaxes rapidly with time. Therefore the shape of the hysteresis loops in PMN and PMN-0.1PT is mainly controlled by the dynamic order parameter.[24] On the contrary, for PMN-0.2PT and PMN-0.29PT the Vogel-Fulcher and Curie temperatures, respectively, lie above room temperature. In this case, the PNRs are in general "frozen" at room temperature, the static order parameter becomes dominant, and the shape of the measured hysteresis loops depends on propagation dynamics of the switched volume underneath of the PFM.[25]

Figure 3 shows the piezoresponse hysteresis loops for the PMN-0.2PT single crystal measured at different temperatures. At high temperatures, especially above T_f, the loops become less saturated and get a "diamond" shape typical for the relaxor state.[24] Both the remanent and saturation piezoresponse attain maximum values at 327 K, which is close to the macroscopic Vogel-Fulcher temperature. At the same time, the positive and negative nucleation biases, i.e., the voltage values corresponding to appearance of a domain with the reversed polarization under the PFM tip,[24] increase gradually with increasing temperature. It should be mentioned that the positive and negative nucleation voltages are nearly equal in magnitude that indicates a negligible impact of built-in fields on polarization switching for this composition.

The initial branches of the local hysteresis loops, i.e., the curves measured starting from the pristine state inside an individual domain by increasing voltage up to U_{max} (Fig. 4) were used to plot temperature dependences of the converse piezoelectric response at different bias fields. The resulting dependences are presented in Fig. 5. At moderate biases two d_{33} maxima are observed: the first slightly below the freezing temperature and the second near the dielectric permittivity peak. At 14 V the high-temperature maximum becomes dominant; however, at higher voltage both maxima merge to a broad one situated at 320 340 K. This transformation is probably the consequence of two processes: the increase of the maximum at T_f on the one hand, and the lowering of T_m with the electric field, which is typical of PMN-xPT,[18] on the other hand. So, at the high bias voltage the position of the

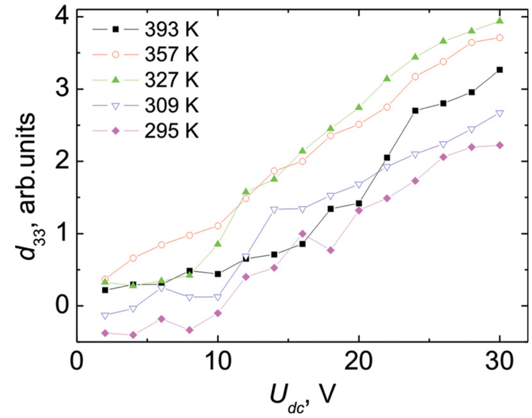

FIG. 4. Field dependencies of the local converse longitudinal piezoresponse for PMN 0.2PT single crystal at different temperatures determined from the initial branches of the hysteresis loops.

local piezoresponse maximum approaches the same temperature range, where the macroscopic $d_{33}(T)$ dependence has a peak at 1.2 kV/cm (Fig. 1(b)).

It has to be mentioned that the observed character of changing of the local piezoresponse maxima with bias voltage is very similar to the field induced evolution of maxima of the pyroelectric coefficient $\gamma(T)$ reported for PMN-xPT crystals and ceramics.[10,11] In particular, for the PMN-0.2PT crystal at low fields also two anomalies were observed on $\gamma(T)$ temperature dependences, which were merged in one broad peak at 330 K under the electric field of $\sim$1.3 kV/cm.[10] Raevskaya *et al*. showed that this field corresponds to the critical point on the (E-T) phase diagram.[10] So, we can consider the observed changes of local $d_{33}(T)$ dependences (Fig. 5) as a manifestation of the critical character of the local piezoresponse in the PMN-PT crystals. The voltage corresponding to the critical point is about 20 V. It is a non-trivial task to calculate the corresponding electric field in the PFM experiment due to strong field inhomogeneity and ill-defined tip-surface interface conditions. Considering the tip as a charged sphere[25] with radius 10 nm, we can roughly estimate that 20 V bias will create at 30 nm depth, approximately in the middle of the probing volume, the electric field about 5 kV/cm. However, this value is evidently overestimated, since the calculation neglects

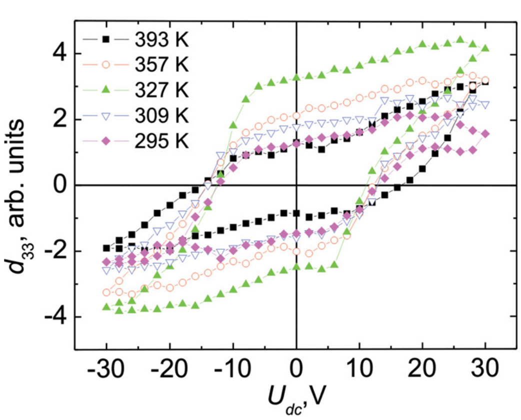

FIG. 3. Local converse longitudinal piezoresponse hysteresis loops for PMN 0.2PT single crystal measured by PFM in the step mode at different temperatures.

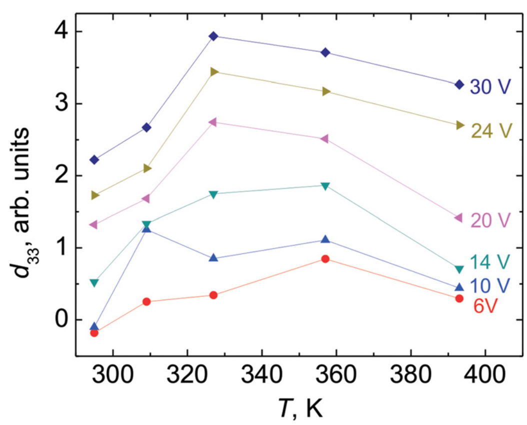

FIG. 5. Temperature dependences of the local converse longitudinal piezor esponse for PMN 0.2PT single crystal at different bias field plotted using the data of Figure 4.

existence of a dielectric gap between tip and sample surface caused, e.g., by the presence of an adsorbate layer on the sample surface, by the depletion phenomenon in doped Si tip, or by a SiO_2 layer on the tip surface.

The attempts to measure the local piezoresponse hysteresis loops at higher bias failed due to the charge injection from the PFM tip into the sample. Such injection, which becomes strong at sufficiently high voltages, results in the development of a space charge region inside the crystal.[26] The formed space charge creates an internal electric field $E_i(r)$, which is directed against the applied field $E(r)$ below the tip. This internal field may induce polarization reversal under the tip after removal of the applied voltage if the charge density is high enough to create $E_i(r)$ exceeding the coercive field in some volume. As the result, after the applied voltage exceeded a certain level, the measured piezoresponse dropped down and became negative. Such artifact effect obscures observation of true field dependence of d_{33} at high biases.

SUMMARY

Both macroscopic direct and local converse longitudinal piezoelectric responses in (001)-oriented flux-grown $(1-x)$ $Pb(Mg_{1/3}Nb_{2/3})O_3$ $xPbTiO_3$ $(0.00 \leq x \leq 0.20)$ single crystals exhibit a dramatic enhancement under a bias field and their maxima shift from the Vogel-Fulcher temperature to the vicinity of the dielectric permittivity maximum, where the critical point in the *E-T* phase diagram is located. These data are in agreement with recent calorimetric and piezoelectric measurements on PMN-0.26PT single crystals[27] as well as with theoretical studies of effect of disorder on critical behaviour in $BaTiO_3$.[28] Obtained results confirm a quasicritical nature of the giant field-induced piezoelectric response in PMN-PT single crystals.

ACKNOWLEDGMENTS

This study was partially supported by the Russian Foundation for Basic Research grant (No. 12-08-01137 a).

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